

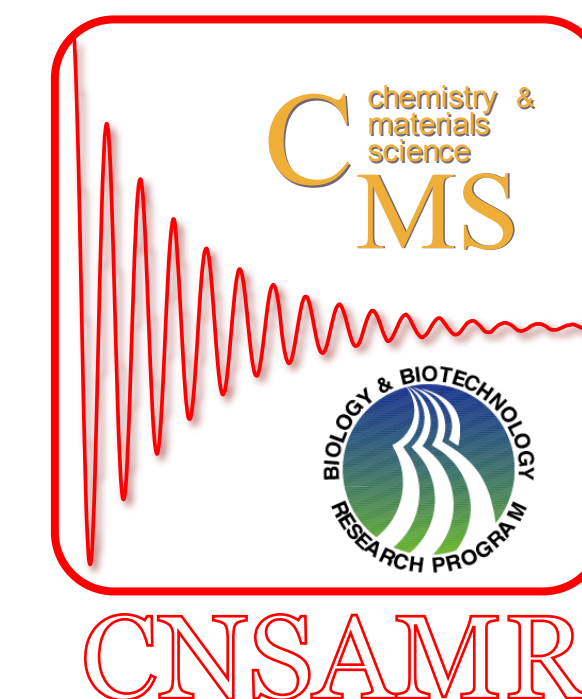


Investigation of Ti-doped NaAlH₄ by solid-state NMR

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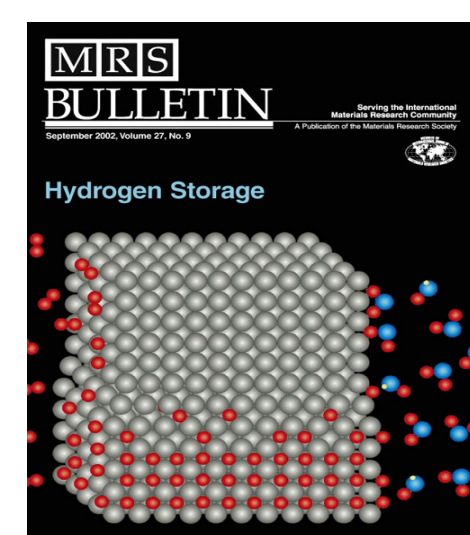


Introduction

Importance of H₂ Storage Technology

Hydrogen Storage / H₂ fuel cells are part of President Bush's initiative to reverse America's growing dependence on foreign oil by developing new energy technologies:

- Overcome key technical and cost barriers for fuel cells
- Hydrogen fuel will help ensure America's energy independence
- Fuel cells will improve air quality and reduce greenhouse gas emissions
- Hydrogen is the key to a clean energy future



To compete with foreign oil as an energy source, we need to produce storage and transportation of hydrogen at or above 62 kg H₂/m³, which is the target set by DOE for the transportation sector

--- Current technology falls short of this target

Current Hydrogen Storage Materials

Metal Hydride Systems

- Metal hydride-nickel hydroxide cells and lithium cells
- Readily absorb large quantities of H₂ at relatively low pressures
- High gravimetric and volumetric energy density to meet the high demands of hydrogen storage for fuel cells (lower efficiency)

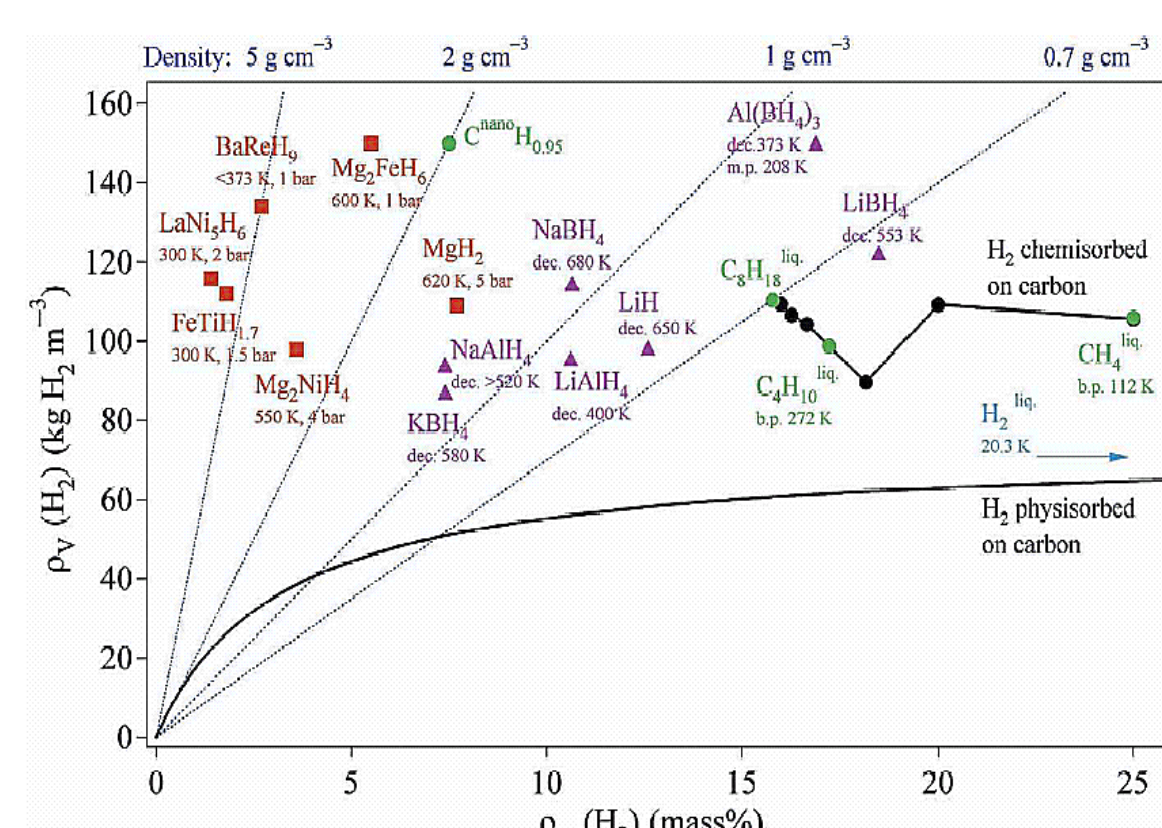
Chemical Hydrides

NaAlH₄, when doped with Ti³⁺, has low gravimetric and volumetric energy density and hydrogen incorporation of ~5 wt. % of H₂

Carbon-based Materials

- Carbon Nanotubes and Nanofibers
- Activated Carbons
- Graphite Intercalation Compounds (K⁺)
- Graphite-Metal Composites (Mg-Ni-C systems)

Opportunities for materials that combine positive aspects of the metal and porous systems



(Reproduced from: Schlöglbach, L. "Hydrogen as a Fuel and Its Storage for Mobility and Transport", MRS proceedings, 2002, Vol. 27, p. 676)

NaAlH₄ as a Material for Hydrogen Storage

Important qualities of hydrogen storage materials used for commercial vehicular applications

- high gravimetric hydrogen density
- hydrogen dissociation energetics
- long-term cyclability
- low cost

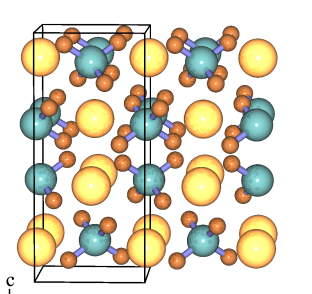
Properties of NaAlH₄ doped with titanium, zirconium, and other catalysts

- 5.0 wt.% hydrogen can be repeatedly cycled through absorption / desorption
- rehydriding only takes 15 min.
- rapid dehydriding occurs at temperatures 100°C
- it is low cost (\$70/kg)

Crystal Structure of NaAlH₄

From both Rietveld refinement of X-ray and neutron powder diffraction data, the NaAlH₄ single crystal structure is revealed.

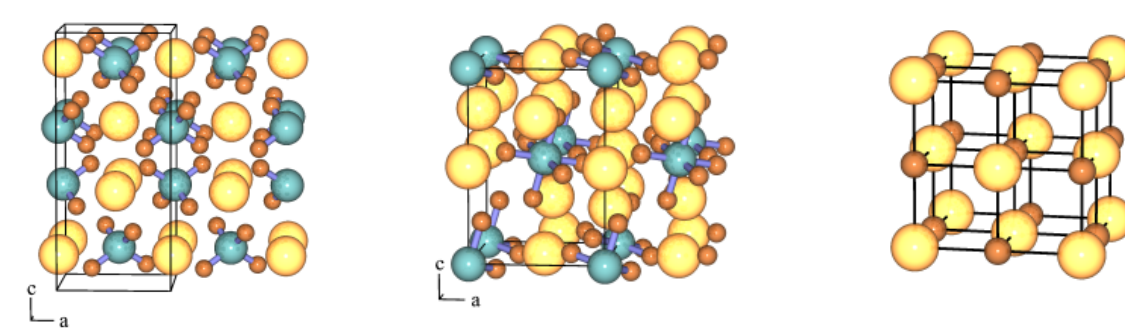
- spacegroup: I4₁/a
- a = 5.02 Angstroms
- c = 11.33 Angstroms
- 1.25 g/cc
- 0.092 g H/cc (liq H₂ 0.07 g/cc)



NaAlH₄

NaAlH₆

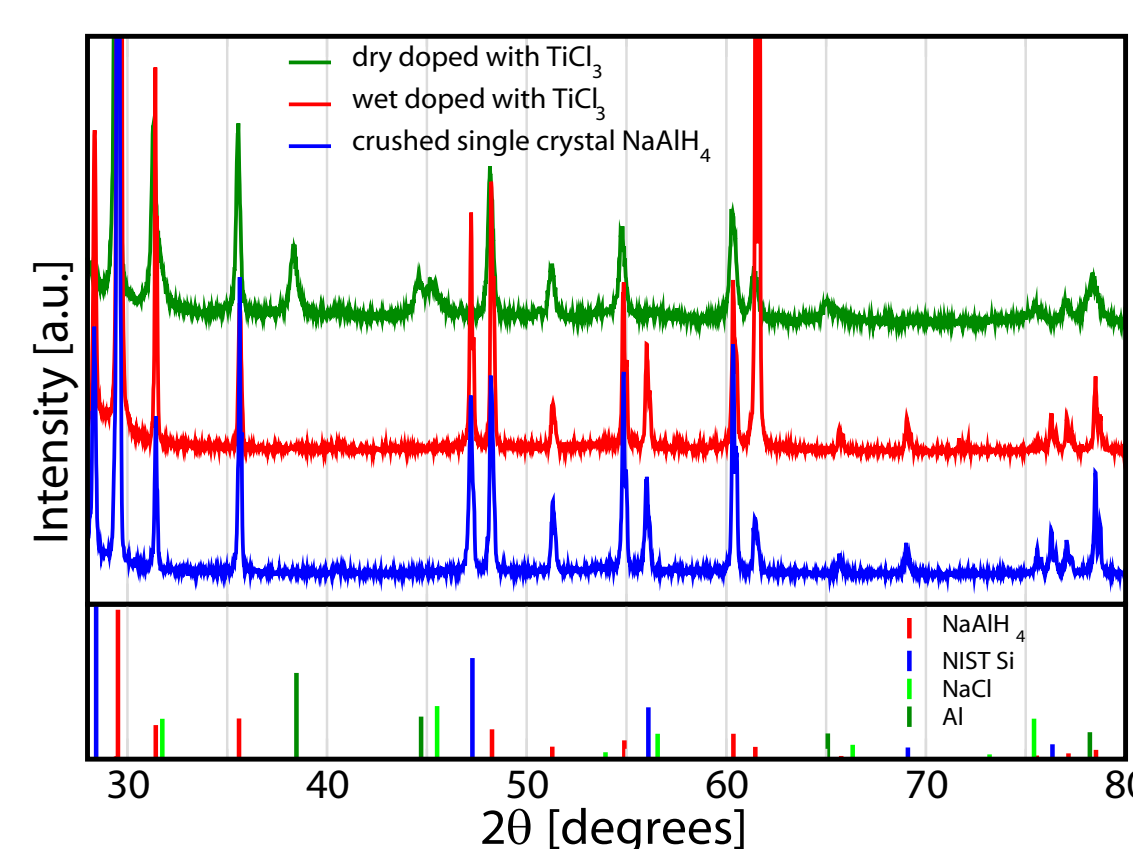
NaH



Transformation Steps

- NaAlH₄ ↔ 1/3 Na₃AlH + 2/3 Al + H₂ **3.7 wt. %**
- NaAlH₆ ↔ 3NaH + Al + 3/2 H₂ **1.9 wt. %**
- Total reversible weight: **5.6 wt. %**
- **3 H's per formula unit**

X-ray Diffraction Data for NaAlH₄ with TiCl₃ and pure NaAlH₄



-Ti Doping has only a small effect on the structure of NaAlH₄.
-Majzoub, E.H. et al. have shown that Al-H bond lengths may be slightly larger due to Ti-doped materials.

Key Question that still need to be answered:
Does there exist structural and dynamical differences between the undoped NaAlH₄ and the Ti doped NaAlH₄ ?

Abstract

In recent years, the development of Ti-doped NaAlH₄ as a hydrogen storage material has gained attention because of its large weight percentage of hydrogen (~5 %), compared to traditional interstitial hydrides. The addition of transition-metal dopants, in the form of Ti-halides, such as TiCl₃, dramatically improve the kinetics of the absorption and desorption of hydrogen from NaAlH₄. X-ray diffraction studies of Sun et al. [1] have suggested that Ti may be substituting into bulk NaAlH₄. These authors, as well as others, have suggested that the Ti is present as Ti³⁺. Desorption kinetics studies by Majzoub et al. [2] have further suggested that the resultant Ti valence state is independent of the precursor Ti-halide used for doping. However, the role that Ti plays in enhancing the absorption and desorption of H₂ is still unknown. In the present study, ²⁷Al, ²³Na, and ¹H MAS NMR have been performed to understand the structural impact that Ti has on the bulk NaAlH₄ material. All experiments were performed with pure NaAlH₄ and NaAlH₄ doped with Ti to fully understand how the Ti impacts this complex network. ²⁷Al-¹H and ²³Na-¹H double resonance experiments were performed to understand structural changes that occur with the addition of the Ti-precursor. Also, T₁, T₂, and multiple quantum ¹H NMR experiments were performed to gather insight into the structure and dynamics of ¹H within Ti-doped NaAlH₄.

[1] D. Sun, T. Kiyobayashi, H.T. Takeshita, N. Kuriyama, C.M. Jensen, *J. Alloys Comp.* 337 (2002) L8-L11

[2] E. H. Majzoub, K.J. Gross, *J. Alloys Comp.*, 1 (2003) in press

Experimental Data

NMR can provide detailed understanding of:

- Structural influence of metal incorporation
- Hydrogen speciation
- Mode of hydrogen interaction (chemi- or physisorbed)
- Release / reversibility mechanisms

We are using NMR methods to examine the structure and dynamics of metal hydride H₂ storage systems.

Description of samples

Fast dried NaAlH ₄	- 1M of NaAlH ₄ dried in THF and vacuum annealed in 10 ⁻⁶ torr - dried fast - possible more mobile hydrogen
Crushed Crystal NaAlH ₄	-crushed single crystals - no Ti ³⁺ present - low mobility of hydrogen
Ti doped NaAlH ₄	-Ti definitely present during crystal formation
(NaAlH ₄) ₁₁₂ + (TiCl ₃) ₄	-NaAlH ₄ is prepared in a TiCl ₃ solution - lots of hydrogen mobility

¹H, ²³Na, and ²⁷Al NMR of NaAlH₄

¹H NMR

²³Na NMR

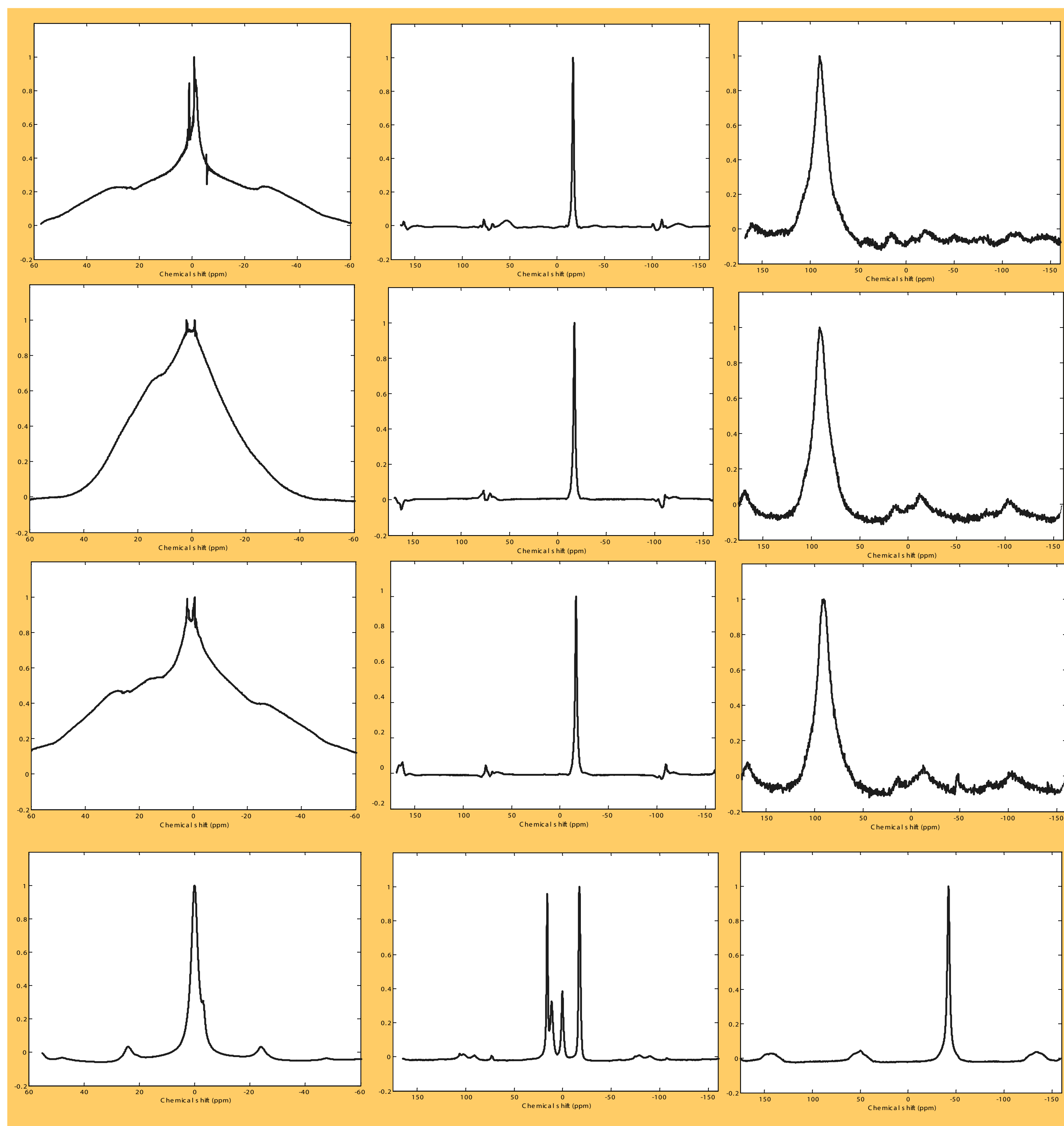
²⁷Al NMR

Fast Dried NaAlH₄

Crushed Crystal NaAlH₄

Ti doped NaAlH₄

(NaAlH₄)₁₁₂ + (TiCl₃)₄



All spectra were acquired at 11.75T with 12kHz MAS

Conclusions

¹H NMR Spectra

- Fast dried NaAlH₄, crushed crystal NaAlH₄, and Ti doped NaAlH₄ ¹H NMR spectra show a broad peak, representing **more clustered hydrogen**, and two narrow peaks, representing **less clustered hydrogen**.
- (NaAlH₄)₁₁₂ + (TiCl₃)₄ ¹H NMR spectra show a narrowing of the broad peak **with the addition of Ti, which might indicate more mobile hydrogen**.

²³Na NMR Spectra

- Fast dried NaAlH₄, crushed crystal NaAlH₄, and Ti doped NaAlH₄ ²³Na NMR spectra show a peak at -17ppm with FWHM of 1.9ppm.
- (NaAlH₄)₁₁₂ + (TiCl₃)₄ ²³Na NMR spectra has four peaks:
 - 1) at 0ppm with a FWHM of 2.3ppm, which represents NaCl₃
 - 2) at -17ppm with a FWHM of 1.9ppm, which represents NaAlH₄
 - 3) & 4) at 15ppm and 12ppm with a FWHM of 1.7ppm and 2.9ppm respectively, which potentially represents NaAlH₄.

²⁷Al NMR spectra

- Fast dried NaAlH₄, crushed crystal NaAlH₄, and Ti doped NaAlH₄ ²⁷Al NMR spectra show a peak at 90ppm with a FWHM of 16ppm.
- (NaAlH₄)₁₁₂ + (TiCl₃)₄ ²⁷Al NMR spectra show a peak at -42ppm with a FWHM of 3ppm. **The narrowing of this lineshape might indicate that the aluminum is mobile with the addition of Ti.**

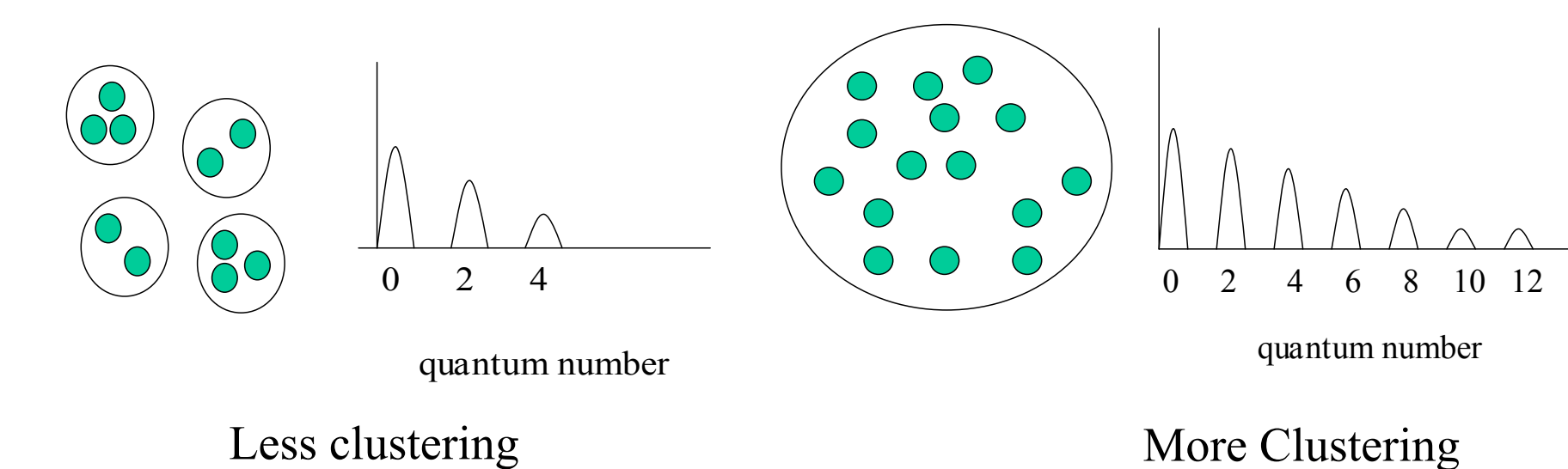
Ti-doped NaAlH₄ is being developed at Sandia National Laboratories as a leading metal hydride material and is an ideal material to analyze the effects of small amounts of metals being incorporated into porous materials, being developed at LLNL.

Future Experiments

1. To understand the dynamical differences in the different materials, we will measure T₁, spin-lattice relaxation time, and T₂, spin-spin relaxation time verses temperature.

2. To understand the difference in ¹H-²³Na and ¹H-²⁷Al bonding mechanism for each materials, we will perform ¹H-²³Na and ¹H-²⁷Al double resonance experiments

3. To further understand ¹H NMR spectra and how protons are clustered within a sample, we will perform multiple quantum experiments.

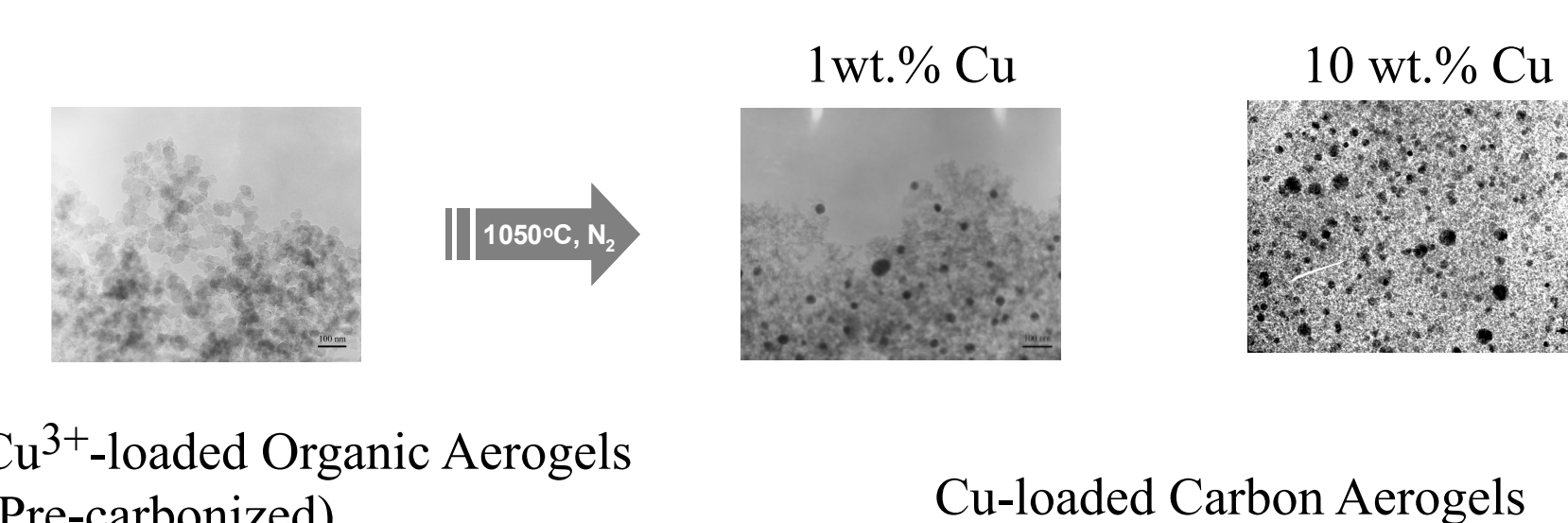


4. We will use these series of experiments to analyze metal-containing **organic and carbon aerogels** for H₂ storage under the guidance of J. Satcher and T. Baumann.

These materials are attractive candidates for H₂ storage due to high surface areas and open porosities.

Theoretically, carbon materials have a **16 wt. %** capacity to store hydrogen, which surpasses any other metal hydrogen system currently used as a hydrogen storage material.

Metallic nanoparticles form during carbonization process:
Particle size: 5 to 60 nm



Cu³⁺-loaded Organic Aerogels (Pre-carbonized)

Cu-loaded Carbon Aerogels